

# PATENT SPECIFICATION

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## (54) NEW 1,3,5-TRIS-(N,N-DIALKYLAMINOALKYL)-S- HEXAHYDROTRIAZINE ADDUCTS AND THEIR USE AS TRIMERIZING CATALYSTS FOR POLYISOCYANATES

(71) We, BASF AKTIENGESSELLSCHAFT, a German joint stock company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

- 5 The present invention relates to new 1,3,5-tris-(N,N-dialkylaminoalkyl)-s-  
 hexahydrotriazine adducts useful as catalysts for the manufacture of polyisocyanurate foams  
 containing urethane groups and polyisocyanates containing isocyanurate groups.  
 The conversion of isocyanates to isocyanurates by means of catalysts has been disclosed.  
 The manufacture of polyisocyanurate foams is also no longer novel.  
 10 The conventional method followed is to cyclize, and polymerize, polyisocyanates in the  
 presence of auxiliaries and catalysts, and to react the resulting isocyanurates containing  
 isocyanate groups, and polymers containing isocyanate groups, with polyols. At times it is also  
 advantageous to carry out the trimerization or polymerization, and the polyaddition of the  
 polyisocyanates and polyols, simultaneously.  
 15 In this context, the polymerization of organic polyisocyanates to give polymerization  
 products having an isocyanurate structure and containing free NCO groups is of particular  
 interest industrially. For this it is necessary to stop the formation of isocyanurate after the  
 desired degree of trimerization or polymerization has been reached. This can be achieved,  
 inter alia, by decomposing or neutralizing the catalysts. Thus, for example, basic catalysts can  
 20 be neutralized by means of acids, e.g. hydrochloric acid.  
 The existing literature describes numerous catalysts for cyclizing and polymerizing  
 isocyanates. Example which may be mentioned are strong bases, such as quaternary  
 ammonium hydroxides, e.g. benzyltrimethylammonium hydroxide, alkali metal hydroxides,  
 e.g. sodium hydroxide or potassium hydroxide, alkali metal alkoxides, e.g. sodium methylate  
 25 and potassium isopropylate, trialkylphosphines, e.g. triethylphosphine,  
 alkylaminoalkylphenols, e.g. 2,4,6-tris-(dimethyl-aminomethyl)-phenol, 3-substituted  
 and/or 4-substituted pyridines, e.g. 3- or 4-methylpyridine, organic-metallic salts, e.g.  
 tetrakis-(hydroxyethyl)-sodium borate, Friedel-Crafts catalysts, e.g. aluminum chloride,  
 iron-(III) chloride, boron fluoride and zinc chloride, and alkali metal salts of weak organic  
 acids and nitrophenolates, e.g. potassium octoate, potassium 2-ethyl-hexoate, potassium  
 benzoate, sodium picrate and potassium-phthalimide. Further trimerizing catalysts are the  
 strongly basic N,N',N''-tris-(dialkylaminoalkyl)-s-hexahydrotriazines, e.g. N,N',N''-tris-  
 (dimethyl-3-aminopropyl)-s-hexahydrotriazine and 2,4,6-tris-(dialkanolamino)-s-triazines,  
 e.g. 2,4,6-tris-(diethanolamino)-s-triazine, as well as mixtures of the said triazine derivatives.  
 35 According to U.S. Patent 2,993,870, various triazine derivatives have proved very  
 successful catalysts for polymerizing aromatic polyisocyanates. Disadvantages of the catalysts  
 described are that some of the compounds are difficult to obtain, that the catalysts only  
 become effective at elevated temperatures, that the formation of isocyanurate is inadequate  
 or that the trimerization and/or polymerization reactions take place too slowly or too rapidly,

i.e. that the course of the reaction cannot be controlled and that it cannot be adapted to suit available machinery and local conditions.

To overcome these disadvantages, German Laid-open application DOS 25 25 017, describes co-catalyst systems for the manufacture of polyisocyanurate foams containing urethane groups, in which systems 1,3,5-tris-(N,N-dialkylaminoalkyl)-s-hexahydrotriazines are mixed with organic monocarboxylic acids or polycarboxylic acids, polyester-ols with acid numbers greater than 4 or half-esters of polycarboxylic acids, in such amounts that the molar ratio of triazine to organic acid component is from 10 : 1 to 1 : 1. Using these co-catalyst systems it is possible to adapt the cream times and rise times, when manufacturing polyisocyanurate foams, to suit the available machinery and local conditions. However, even these co-catalyst systems in some cases do not satisfy all the requirements they have to meet. Since the co-catalyst systems are mixtures of compounds, their metering into other starting materials at times presents certain difficulties. A further disadvantage is that the free acids in some cases slowly react with isocyanates.

The present invention seeks to provide processes for the trimerization and/or polymerization of polyisocyanates, which make it possible to vary the cream times and rise times, when manufacturing polyisocyanurate foams containing urethane groups, within certain limits, and which furthermore make it possible to manufacture polyisocyanates, containing isocyanurate groups, which have defined free NCO contents, and which do not possess the above disadvantages. The cream time is to be understood as the time required to arrive at a foamable mixture which can be poured satisfactorily, i.e. the time available between mixing the components and the start of a visible reaction, during which time the mixing of the starting materials, the discharge from the mixing equipment and the pouring of the reaction mixture have to be completed. The rise time is defined as the time, counted from the start of the mixing operation, required to reach the maximum volume of foam.

We have found, surprisingly, that good results may be achieved by using a new catalyst which makes it possible to manufacture polyisocyanurate foams, containing urethane groups, which have a uniform fine-cell pore structure, a low brittleness and excellent mechanical properties, in particular very good compressive strength and flexural strength.

According to the present invention there is provided an adduct of  
a) one mole of 1,3,5-tris-(N,N-dialkylaminoalkyl)-s-hexahydrotriazine and  
b) from 5.5 to 6 equivalents of OH-acidic organic compound having a pKa of from 3 to 10 measured at 20° to 25°C.

The adducts are defined chemical compounds (salts) and have the advantages, compared to 1,3,5-tris-(N,N-dialkylaminoalkyl)-s-hexahydrotriazines and co-catalyst systems of 1,3,5-tris-(N,N-dialkyl-aminoalkyl)-s-hexahydrotriazines and carboxylic acids, as described in German Laid-open application DOS 25 25 017, that they are in general more active as catalysts. For the manufacture of polyisocyanurate foams, i.e. that for the same reactivity of the polyisocyanurate foam systems, less catalyst is required or that identical amounts of catalyst give shorter cream times and rise times, that systems which contain polyol, flameproofing agent, especially tris-B-chloroethyl phosphate, auxiliaries and additives, in general, have a better shelf life in the presence of the adducts as catalysts than of prior art catalysts, and that the polyisocyanurate foam systems exhibit improved flow, so that the formulations are suitable for a broader range of uses and in particular can be employed in cases where long flow paths are needed. Furthermore, when using one of the new adducts as catalyst, the preparation of polyisocyanurate foam systems with short cream times presents no problems.

The adducts preferred as catalysts consist, for example, of 1,3,5-tris-(N,N-dimethylamino-propyl)-s-hexahydrotriazine, 6 formic acid, 1,3,5-tris-(N,N-diethylaminopropyl)-s-hexahydrotriazine, 6 acetic acid, 1,3,5-tris-(N,N-dimethylaminopropyl)-s-hexahydrotriazine, 6 2-ethyl-hexanoic acid, 1,3,5-tris-(N,N-dimethyl-aminopropyl)-s-hexahydrotriazine, 6 benzoic acid, 1,3,5-tris-(N,N-dimethylaminoethyl)-s-hexahydrotriazine, 3 succinic acid, 1,3,5-tris-(N,N-dimethylaminopropyl)-s-hexahydrotriazine, 3 succinic acid, 1,3,5-tris-(N,N-dimethylaminopropyl)-s-hexahydrotriazine, 3 adipic acid and 1,3,5-tris-(N,N-dimethyl-aminopropyl)-s-hexahydrotriazine, 6 2,4,6-trichlorophenol. An adduct having the composition 1,3,5-tris-(N,N-dimethylaminopropyl)-s-hexahydrotriazine, 6 acetic acid has proved particularly suitable and is therefore preferred.

Examples of 1,3,5-tris-(N,N'-dialkylaminoalkyl)-s-hexahydrotriazines for the manufacture of an adduct within the invention are, 1,3,5-tris-(N,N-dimethyl-2-aminoethyl)-s-hexahydrotriazine, 1,3,5-tris-(N,N-dimethyl-3-aminopropyl)-s-hexahydrotriazine, 1,3,5-tris-(N,N-diethyl-2-aminoethyl)-s-hexahydrotriazine, 1,3,5-tris-(N,N-diethyl-3-aminopropyl)-s-hexahydrotriazine and 1,3,5-tris-(N,N-dipropyl-2-aminoethyl)-s-hexahydrotriazine. However 1,3,5-tris-(N,N-dimethyl-3-aminopropyl)-s-hexahydrotriazine is preferred for the purposes of the present invention.

Thus hexahydrotriazine components and their manufacture are known and are described, for example, by Nicholas et al, Journal of Cellular Plastics / (1) (1965), 85 and by Graymore,

Journal of the Chemical Society (1931), 1,493.

As already mentioned, the other component of the adduct consists of an OH-acidic organic compound having a pKa of from 3 to 10, preferably from 4 to 6, measured at 20° to 25°C (see Handbook of Chemistry and Physics, 50th Edition).

OH-acidic organic compounds having a pKa in the above range which may be used with advantage are substituted phenols, e.g. phenols substituted by nitro groups and/or halogen, e.g. chlorine, atoms, and preferably, organic carboxylic acids, e.g. cycloaliphatic, aromatic and/or especially aliphatic monocarboxylic acids and/or polycarboxylic acids. Specific examples of substituted phenols are nitrophenols, e.g. 2,4- and 3,6-dinitrophenol and o-, m- and p-nitrophenol, but chlorophenols, e.g. 2,3-dichlorophenol and especially 2,4,6-trichlorophenol.

Examples of suitable organic carboxylic acids are cycloaliphatic monocarboxylic acids and polycarboxylic acids, e.g. cyclohexanemonocarboxylic acids and ortho-cyclohexanedicarboxylic acid, aromatic monocarboxylic acids and polycarboxylic acids, e.g. terephthalic acid and especially benzoic acid and, preferably, aliphatic monocarboxylic acids and polycarboxylic acids, e.g. formic acid, butyric acid, valeric acid, 2-ethyl hexanoic acid, succinic acid, adipic acid and, preferably, acetic acid. To manufacture an adduct within the invention, the 1,3,5-tris-(N,N-dialkylaminoalkyl)-s-hexahydrotriazine(s) and OH-acidic organic compound(s) having a pK of from 3 to 10 are mixed in proportions sufficient to provide from 5.5 to 6, preferably about 6, equivalents of OH-acidic organic compound per mole of triazine in the reaction mixture. The reaction is advantageously carried out at from 0°C to 60°C, preferably at from 20 to 40°C, in the presence of an inert solvent or, if both starting components are liquid, preferably in the absence of inert solvents. Examples of inert solvents are acetone, acetonitrile, ethyl acetate and, preferably, dimethylformamide. The new adducts can in some cases be isolated by allowing them to crystallize out, and in some cases by removing the solvent or by precipitating the product.

The adducts according to the invention are oily substances or crystalline compounds which may be characterized by, for example, elementary analysis.

By using an adduct within the invention as the catalyst it proves possible to trimerize and/or polymerize organic polyisocyanates, especially aliphatic diisocyanates, in a simple manner.

Accordingly, the present invention also provides a process for the manufacture of a polyisocyanurate foam which contains urethane groups, and which may or may not be of low flammability, by reacting an organic polyisocyanate and a polyol in the presence of a catalyst and in the presence or absence of a blowing agent and other auxiliaries and additives, wherein the catalyst used comprises an adduct of one mole of 1,3,5-tris-(N,N-dialkylaminoalkyl)-s-hexahydrotriazine and from 5.5 to 6 equivalents of OH-acidic organic compound having a pKa of from 3 to 10 measured at 20° to 25°C.

In general, from 0.5 to 10 parts by weight, preferably from 1 to 3 parts by weight, of new adducts, is used as catalyst, per 100 parts by weight of organic polyisocyanate, to manufacture the polyisocyanurate foam which contains urethane groups and may or may not be of low flammability.

In addition to an adduct within the invention it is in many cases useful to employ, as an additional catalyst, a compound which accelerates the formation of a polyurethane from a polyol and a polyisocyanate. Examples of suitable catalysts are tert.-amines, e.g. 1,4-diazabicyclo-(2,2,2)-octane and N,N-dimethylbenzylamine, certain organic metal compounds, such as stannous-octoate and dibutyl-tin dilaurate, and mixtures of tertiary amines and tin compounds.

Examples of polyisocyanates for manufacturing the polyisocyanurate foams, which foams contain urethane groups and may or may not be of low flammability, are organic polyisocyanates of the formula



where R is a polyvalent aliphatic, alkylaromatic or aromatic organic radical, and n is an integer, the value of which corresponds to the valency of R and is at least two. Typical organic polyisocyanates suitable for the purposes of the invention include, for example, aromatic polyisocyanates, e.g. 2,4- and 2,6-toluylene diisocyanate, 2,2'-, 2,4'-diphenylmethane diisocyanate, triphenylmethane triisocyanates, biphenyl diisocyanates, m- or p-phenylene diisocyanate, 1,5-naphthylene diisocyanate and aliphatic polyisocyanates, e.g. isophorone diisocyanate and hexamethylene diisocyanate. The use of crude and pure toluylene diisocyanates and of mixtures of 2,2'-, 2,4'- and 4,4'-diphenylmethane diisocyanate and polyphenyl-polymethylene polyisocyanates is preferred. The polyisocyanates may be used individually or as mixtures.

Polyisocyanurate foams may be manufactured with or without the use of polyols. If the conventional catalysts are used in the absence of polyols, predominantly brittle foams are obtained, which in most cases are useless for industrial applications. For this reason, polyols are used as an additional starting material in the present process when manufacturing

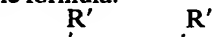
polyisocyanurate foams in the presence of the adducts of the invention as catalysts.

Examples of polyols which may be used for the manufacture of the polyisocyanurate foams according to the present process which contain urethane groups, are monomeric polyols, e.g. ethylene glycol, propylene glycol, 1,4-butanediol, trimethylolpropane, pentaerythritol, sugar alcohols, sucrose and, preferably, polyols of relatively high molecular weight, e.g. polyetherols and/or polyesterols.

Suitable polyetherols may be manufactured by reacting one or more alkylene oxides, where alkylene is of 2 to 4 carbon atoms, with a starter molecule which contains several chemically bonded active hydrogen atoms. Examples of suitable alkylene oxides are ethylene oxide, 1,2-propylene oxide, epichlorohydrin, 1,2-butylene oxide and 2,3-butylene oxide. The alkylene oxides may be used individually, or in alternating succession, or as mixtures. Examples of suitable starter molecules are water, phosphoric acid, amines e.g. ammonia, hydrazine, ethylenediamine, hexamethylenediamine, toluylenediamine, diamino-phenylmethane and melamine, amino-alcohols, e.g. monoethanolamine and diethanolamine, polycarboxylic acids, e.g. adipic acid, tetrachlorophthalic acid, tetrabromophthalic acid and terephthalic acid, and polyhydroxy compounds, e.g. ethylene glycol, propylene glycol, diethylene glycol, glycerol, trimethylolpropane, pentaerythritol, sorbitol and sucrose. The polyalkylene-ethers, which may have straight, partially branched or completely branched chains, have molecular weights of from 300 to 10,000, preferably from 400 to 3,000 and hydroxyl numbers from 30 to 800, preferably from 35 to 400.

Suitable polyester-polyols may be manufactured from, for example, dicarboxylic acids and polyhydric alcohols. Examples of suitable dicarboxylic acids are aliphatic dicarboxylic acids, e.g. succinic acid, glutaric acid, adipic acid, suberic acid, azeleic acid and sebacic acid, and aromatic dicarboxylic acids, e.g. phthalic acid, isophthalic acid and terephthalic acid. The acids may be used individually or as mixtures. When manufacturing the polyesterols it may at times be advantageous to replace the carboxylic acids by corresponding carboxylic acid derivatives, e.g. carboxylic acid esters with alcohols of 1 to 4 carbon atoms, carboxylic acid anhydrides or carboxylic acid chlorides. Examples of polyhydric alcohols are glycols, e.g. ethylene glycol, diethylene glycol, 1,4-butanediol, 1,5-pentane-diol, 1,6-hexanediol, 1,10-decanediol, 2,2-dimethyl-1,3-propanediol and 2,2,4-trimethyl-1,3-pentanediol, triols, e.g. glycerol and trimethylolpropane, and polyols, e.g. pentaerythritol, sorbitol and sucrose. Depending on the desired properties, the polyols may be employed individually or as mixtures in varying ratios. The polyester-polyols, which may have straight or branched chains and may be difunctional or polyfunctional, have molecular weights of from 500 to 5,000, preferably from 800 to 3,000, and hydroxyl numbers of from 30 to 500, preferably from 40 to 250.

Polyesterols which are particularly suitable and used preferentially for the manufacture of polyisocyanurate foams which contain urethane groups and are of low flammability, are those which are manufactured by condensing aliphatic dicarboxylic acids of 4 to 12 carbon atoms and a diol mixture of aliphatic diols of 2 to 18 carbon atoms, which may or may not be substituted and/or may not contain ether groups, and halogen-substituted aromatic diols of the formula:



where A is a halogen-substituted phenylene, naphthylene or diphenylene radical, R is an aliphatic radical of 1 to 4 carbon atoms which may or may not be substituted but contains at least one chemically bonded hydroxyl group and R' is hydrogen or an aliphatic radical of from 1 to 4 carbon atoms, which may or may not be substituted. Such polyesterols, which have molecular weights of from 800 to 3,000, preferably from 800 to 2,000 and hydroxyl numbers of from 140 to 35, preferably from 140 to 56, are disclosed in our copending British Patent Application No. 33142/75 (Patent Specification 1507557).

Blowing agents, which may or may not be employed in the present process, include water, which reacts with isocyanate groups to form carbon dioxide. The amounts of water which may advantageously be used are from 0.1 to 2% based on the weight of polyisocyanate. However, at times larger amounts of water may also be used, though this is preferably avoided if the heat stability or heat insulating properties are of particular importance.

Other blowing agents which may be used are low-boiling liquids which vaporize under the influence of the exothermic polymerization reaction. Suitable liquids are those which are inert towards the organic polyisocyanate and have boiling points not exceeding 100°C, and preferably of from -40 to +50°C, under atmospheric pressure. Examples of such preferred liquids are halohydrocarbons, e.g. methylene chloride, trichlorofluoromethane, dichlorofluoromethane, dichloromonofluoromethane, dichlorotetrafluoroethane and 1,1,2-trichloro-1,2,2-trifluoroethane. Mixtures of these low-boiling liquids with one another and/or with other substituted or unsubstituted hydrocarbons may also be used.

The most appropriate amount of low-boiling liquid used to manufacture semi-rigid and rigid

foams depends on the desired foam density and on whether water is also present. In general, amounts of from 5 to 40 per cent by weight, based on organic polyisocyanate, give satisfactory results.

5 The reaction mixture may also contain auxiliaries and additives. Examples include stabilizers, agents to afford protection against hydrolysis, pore regulators, fungistatic and bacteriostatic agents, dyes, pigments, fillers, surface-active compounds, plasticizers and flameproofing agents. 5

10 By way of example, surface-active compounds which may be used are those which serve to assist the homogenizing of the starting materials and which may also be capable of regulating the cell structure of the foams. Examples which may be mentioned are siloxane-oxyalkylene copolymers and other organopolysiloxanes, oxyethylated alkylphenols, oxyethylated fatty alcohols, paraffin oils, castor oil esters and ricinoleic acid esters, and turkey red oil; they are used in amounts of from 0.2 to 6 parts by weight per 100 parts by weight of polyisocyanate. 10

15 It may also be advantageous to include a plasticizer in the reaction mixture so as to reduce the brittleness of the products. Conventional plasticizers may be used, but it is particularly advantageous to use those which contain phosphorus and/or halogen and as a result additionally reduce the flammability of the polyisocyanurate foams. Such agents include tricresyl phosphate, tris-2-chloroethyl phosphate, tris-chloropropyl phosphate and tris-2,3-dibromopropyl phosphate. 15

20 In addition to the above halogenated phosphates, inorganic flame-proofing agents, e.g. antimony trioxide, arsenic oxide, ammonium phosphate and calcium sulfate, may also be used to flameproof the polyisocyanurate foams containing urethane groups. In general, it has proved advantageous to employ from 5 to 50 parts by weight, preferably from 5 to 25 parts by weight, of the said flameproofing agents per 100 parts by weight of organic polyisocyanate. 20

25 The polyisocyanurate foams containing urethane groups are manufactured by the prepolymer process or, preferably, by the one-shot process. For this purpose, the polyisocyanates are reacted with polyols at from 10 to 50°, preferably from 15 to 28°C, in ratios such as to provide from 6 to 60, preferably from 10 to 40, NCO groups of the polyisocyanate per hydroxyl group of the polyol, in the reaction mixture. If a mixing chamber with several feed nozzles is used, the polyisocyanate, the polyol, the catalyst and — where relevant — the blowing agent, the auxiliaries and the additives, may be fed in individually and mixed thoroughly in the mixing chamber. However, it is also possible first to mix the catalyst, the blowing agent, the auxiliaries and the additives with one of the main components, i.e. the polyisocyanate or the polyol, and then to mix this product mixture thoroughly with either the polyol or the polyisocyanate in the mixing chamber, and allow the foamable mixture to rise. 25

30 The polyisocyanurate foams, containing urethane groups, manufactured in accordance with the invention have densities of from 15 to 400 kg/m<sup>3</sup>, preferably from 30 to 80 kg/m<sup>3</sup>, and are distinguished by a uniform fine-cell pore structure, low brittleness, excellent mechanical properties, very good heat stability and, in appropriate cases, non-flammability. The products may be used as, for example, insulating materials. 30

40 The invention further provides a process for the manufacture of a polyisocyanate containing isocyanurate groups, by trimerising or polymerising an aliphatic and/or an aromatic polyisocyanate in the presence of a catalyst which is an adduct of 40

- 45 a) one mole of 1,3,5-tris-(N,N-dialkylaminoalkyl)-s-hexahydrotriazine and  
b) from 5.5 to 6 equivalents of OH-acidic organic compound having a pK<sub>a</sub> of from 3 to 10 measured at 20° to 25°C. 45

Surprisingly, we have found that using an adduct within the invention as catalyst, even aliphatic diisocyanates can be trimerized and/or polymerized under mild reaction conditions.

50 In general, from 0.5 to 10, preferably from 1 to 3, parts by weight of the adducts according to the invention are used as the catalyst, per 100 parts by weight of organic diisocyanate, in order to manufacture the polyisocyanates containing isocyanurate rings. 50

55 The new adducts employed for the manufacture of polyisocyanates containing isocyanurate rings are preferably used for trimerizing and/or polymerizing aliphatic diisocyanates. However, it is also possible to trimerize or polymerize mixtures of aliphatic and aromatic diisocyanates conjointly. The adducts are advantageously used as catalysts in cases where the molar ratio of aliphatic to aromatic diisocyanates is from 0.2 to 5, preferably from 0.5 to 3. 55

60 Examples of aliphatic diisocyanates which can be polymerized with the aid of the new adducts are butane diisocyanate, pentane diisocyanate, heptane diisocyanate, cyclohexane 1,4-diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (isophorone diisocyanate), 2,2,4-trimethylhexamethylene diisocyanate and, preferably, hexamethylene 1,6-diisocyanate. Such diisocyanates are described, for example, in Liebig's Ann. d. Chemie 562 (1949), 121 et seq. Examples of aromatic diisocyanates which can be trimerized and/or polymerized separately or conjointly with the aliphatic diisocyanates are m- and p-phenylene diisocyanate, 2,4- and 2,6-toluylene diisocyanate and 2,4-, 2,2- and 4,4'-diphenylmethane diisocyanate. Preferably, mixtures of hexamethylene diisocyanate and 2,4- and/or 65 65

2,6-toluylene diisocyanate and mixtures of hexamethylene diisocyanate and 4,4'-diisocyanato-diphenylmethane are trimerized and/or polymerized.

To manufacture the polyisocyanate(s) containing isocyanurate groups, the catalyst is added to the aliphatic diisocyanate(s), or aromatic diisocyanate(s) or mixture of aliphatic and aromatic diisocyanates, at from 0°C to 150°C; the reaction is then allowed to take place at these temperatures, but preferably at from 20 to 80°C, especially at from 30 to 60°C, until the desired NCO number is reached. Usually, the reaction time is from 0.1 to 16 hours, preferably from 1 to 4 hours. The trimerization and/or polymerization may be carried out in the absence or presence of organic solvents. Suitable solvents are those which do not react with isocyanates, e.g. methylene chloride, chloroform, chlorobenzene, acetone, methyl ethyl ketone, ethyl acetate, butyl acetate, tetrahydrofuran, dioxane, toluene and xylene.

When the desired NCO number has been reached, the reaction is stopped by adding a suitable compound which deactivates the catalyst. Suitable deactivating agents include strong acids or carboxylic acid halides. By way of example, phosphoric acid and hydrochloric acid may be mentioned as acids and acetyl chloride, benzoyl chloride and toluenesulfonyl chloride may be mentioned as carboxylic acid halides. In general, the trimerization and/or polymerization reaction is effectively terminated by adding from about 1 to 20 equivalents of acid and/or carboxylic acid halide per equivalent of catalyst.

After stopping the reaction, the unconverted monomeric diisocyanates, and any solvents which may have been used, can be removed under mild conditions. This may be achieved by a high vacuum distillation in suitable evaporators, or by extraction with suitable solvents in which only the monomeric diisocyanates, but not the trimeric and/or polymeric polyisocyanates, are soluble, e.g. with aliphatic or cycloaliphatic hydrocarbons.

The polyisocyanates, containing isocyanurate groups, manufactured using an adduct according to the invention as catalyst have total NCO contents of from 20 to 40%. They are resins which are solid at room temperature or viscous liquids, both the resins and viscous liquids being soluble in a number of organic solvents. Such solvents include, for example, ethyl acetate, butyl acetate, ethyl glycol ether acetate, acetone, cyclohexanone, methylene chloride and chlorobenzene.

The polyisocyanates containing isocyanurate groups are valuable starting materials for the manufacture of polyester and polyether finishes, one-component polyurethane finishes, polyurethane casting resins, polyurethane elastomers, polyurethane foams and polyurethane adhesives.

In the examples, parts are by weight.

#### Examples 1 to 9

General instructions for the manufacture of the adducts according to the invention.

6 equivalents of the OH-acidic organic compound are added dropwise to one mole of 1,3,5-tris-(N,N-dialkylaminoalkyl)-s-hexahydrotriazine whilst stirring and cooling to below 40°C. In the case of solid OH-acidic organic compounds, a saturated solution in dimethylformamide is prepared before the reaction. The reaction has ended when all the material has been added. If the starting components are employed in non-equivalent amounts, this manifests itself in the formation of two phases. If the reaction is carried out in the presence of solvents, the latter are distilled off under reduced pressure. The adducts according to the invention can be purified by extraction with non-polar solvents, e.g. ethers, carbon tetrachloride or hexane.

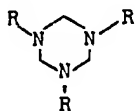
The starting components used to manufacture the adducts according to the invention, the ratios employed, the solvent, if any, and the end products obtained are shown in Table 1.

Table 1

Manufacture of the adducts according to the invention:  
 Example s-hexahydrotriazine OH-acidic compound

Solvent

Adduct



R

		Amount (moles)	Nature	Amount (moles)	Nature	
1	CH <sub>3</sub> \ N-(CH <sub>2</sub> ) <sub>3</sub> -	1	acetic acid	6	—	—
	CH <sub>3</sub> /					
2	CH <sub>3</sub> \ N-(CH <sub>2</sub> ) <sub>3</sub> -	1	formic acid	6	—	—
	CH <sub>3</sub> /					
3	CH <sub>3</sub> \ N-(CH <sub>2</sub> ) <sub>3</sub> -	1	2-ethylhexanoic acid	6	—	—
	CH <sub>3</sub> /					
4	CH <sub>3</sub> \ N-(CH <sub>2</sub> ) <sub>3</sub> -	1	benzoic acid	6	dimethyl- formamide	57% by weight strength solution
	CH <sub>3</sub> /					
5	CH <sub>3</sub> \ N-(CH <sub>2</sub> ) <sub>3</sub> -	1	succinic acid	3	dimethyl formamide	53% by weight strength solution
	CH <sub>3</sub> /					

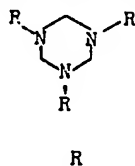
*Table 1 (Continuation)*  
 Elementary analysis of the adduct consisting of  
 one mole of s-hexahydrotriazine and  
 6 equivalents of the OH-acidic organic compound

Example	C		H		O		N		Melting point	Viscosity 25°C	Refractive index nd 20°C
	calc. %	found %	calc. %	found %	calc. %	found %	calc. %	found %			
1	51.2	51.2	9.5	9.4	27.3	28.1	12	11.6	155-165°C with decomp.	1,350	1.4757
2	46.6	46.2	8.8	9.2			13.6	13.6	30-35°C	260	1.4902
3	67.0	66.6	11.6	11.5			6.5	6.3	with decomp. 200-210°C	2,500	1.4647
4	59.4	59.1	8.3	8.5			12.8	12.9	with decomp. —	13	—
5	50.6	50.2	9.1	9.4			15.4	15.1	—	73	—



Table 1 (continuation)

Manufacture of the adducts according to the invention:  
 Example s-hexahydrotriazine OH-acidic compound



Solvent

Adduct

	Amount (moles)	Nature	Amount (moles)	Nature	
6 $\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \text{N}-(\text{CH}_2)_3-$	1	adipic acid	3	dimethyl- formamide	56% by weight strength solution
7 $\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \text{N}-(\text{CH}_2)_3-$	1	2,4,6-trichloro- phenol	6	diethyl formamide	67% by weight strength solution
8 $\begin{array}{c} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \text{N}-(\text{CH}_2)_3-$	1	acetic acid	6	—	—
9 $\begin{array}{c} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \text{N}-(\text{CH}_2)_2-$	1	acetic acid	6	—	—

*Table 1 (Continuation)*  
 Elementary analysis of the adduct consisting of  
 one mole of s-hexahydrotriazine and  
 6 equivalents of the OH-acidic organic compound

Example	C			H			O			N	Melting point	Viscosity 25°C	Refractive index nd 20°C
	calc. %	found %	calc. %	found %	calc. %	found %	calc. %	found %	calc. %				
6	52.7	52.2	9.4	9.2					14.5	14.2	—	12	—
7	44.7	44.4	5.8	5.9					10.0	10.1	—	190	—
8	53.1	53.0	9.6	9.2					11.3	11.5	170-178°C	4,340	1.4647
9	54.9	55.1	9.9	9.8					10.6	10.3	with decomp. 158-165°C with decomp.	4,460	1.4728

*Examples 10 to 15*

In order to determine the activity of the catalyst by the exotherm test, the adducts, dissolved in 5 ml of dimethylformamide, are reacted with 80 g of 4,4'-diphenylmethane diisocyanate at room temperature. The exothermic isocyanurate formation is followed by measuring the temperature. The catalysts used are adducts of 1,3,5-tris-(N,N-dimethylaminopropyl)-s-hexahydrotriazine (HHT). The results of the measurements are shown in Table 2.

Table 2 Example	Catalyst Nature	Amount [g]	pK of the OH-acidic compound	Time to reach the maximum exotherm, R max [sec]	Maximum temperature rise $\Delta t$ [°C]
19	HHT . 6 acetic acid	0.5	4.75	90	81.4
11	HHT . 6 formic acid	0.45	3.75	95	83.6
12	HHT . 6 2-ethyl hexanoic	0.9	4.8	250	71.7
13	HHT . 6 benzoic acid	0.8	4.2	470	97.5
14	HHT . 3 adipic acid	0.55	4.4	200	78.5
15	HHT . 6 2,4,6-trichlorophenol	1.1	6.0	260	60.5
comparative examples	HHT	0.25	—	680	58
	HHT	0.5	—	550	80

*Examples 16 to 24*

General instructions for the manufacture of polyisocyanurate foams containing urethane groups:

- 5 40 g of a mixture of diisocyanatodiphenylmethanes and polyphenyl-polymethylene polyisocyanates are added, whilst stirring at room temperature, to a mixture of 8 g of polyol, 8 g of tris- $\beta$ -chloroethyl phosphate, X g of the adduct according to the invention, 0.5 g of a siloxane-polyoxyalkylene copolymer (product DC 193 from Dow Corning Corp.) and 10 g of trichlorofluoromethane. 5
- 10 The foamable mixture is then allowed to foam in a conical 1,000 ml beaker having a bottom diameter of 8 cm and a top diameter of 12 cm, and the cream times and rise times are observed. 10
- 15 The nature and amount of the adduct according to the invention, used as the catalyst (the 1,3,5-tris-(N,N-dialkylaminoalkyl)-s-hexahydrotriazine used was 1,3,5-tris-(N,N-dimethylaminopropyl)-s-hexahydrotriazine (HHT) in every example), the nature of the polyol and the cream times and rise times observed are shown in Table 3. 15

**Table 3**  
**Manufacture of polyisocyanurate foams containing urethane groups:**  
**Example Adduct (used as the catalyst) Nature Amount [g]**

Example	Adduct (used as the catalyst) Nature	Amount [g]	Polyol	Rise time [sec]	Cream time [sec]
16	HHT . 6 acetic acid	1	Adipic acid/diethylene glycol/N,N'-bis-(ethanol-2)-diaminooctachlorodiphenyl polyester, molecular weight about 2,000	12	55
17	HHT . 6 formic acid	0.9	Adipic acid/diethylene glycol/N,N'-bis-(ethanol-2)-diaminooctachlorodiphenyl polyester, molecular weight about 2,000	53	90
18	HHT.6 2-ethyl hexanoic acid	1.9	Adipic acid/diethylene glycol/N,N'-bis-(ethanol-2)-diaminooctachlorodiphenyl polyester, molecular weight about 2,000	8	85
19	HHT . 6 2,4,6-trichlorophenol	5.7	Adipic acid/diethylene glycol/N,N'-bis-(ethanol-2)-diaminooctachlorodiphenyl polyester, molecular weight about 2,000	4	84
21	HHT . 6 acetic acid	1	Adipic acid/diethylene glycol/N,N'-bis-(ethanol-2)-diaminooctachlorodiphenyl polyester, molecular weight about 2,000	8	73
22	HHT . 6 acetic acid	1	Adipic acid/diethylene glycol/N,N'-bis-(ethanol-2)-diaminooctachlorodiphenyl polyester, molecular weight about 2,000	15	100
23	HHT . 6 acetic acid	1	Adipic acid/diethylene glycol/N,N'-bis-(ethanol-2)-diaminooctachlorodiphenyl polyester, molecular weight about 2,000	12	85
24	HHT . 6 acetic acid	1	Adipic acid/diethylene glycol/N,N'-bis-(ethanol-2)-diaminooctachlorodiphenyl polyester, molecular weight about 2,000	8	68
Comparative Example	HHT	0.5	Adipic acid/diethylene glycol/N,N'-bis-(ethanol-2)-diaminooctachlorodiphenyl polyester, molecular weight about 2,000	190	500
Comparative Example	HHT	1.2	Adipic acid/diethylene glycol/N,N'-bis-(ethanol-2)-diaminooctachlorodiphenyl polyester, molecular weight about 2,000	100	320

*Examples 25 to 30*

General instructions for the manufacture of polyisocyanates containing isocyanurate groups.

5 150 g of hexamethylene diisocyanate are trimerized with X g of the adduct according to the invention, as the catalyst, at 50°C. This caused a progressive fall in the NCO content of the reaction mixture from about 50%. The trimerization is stopped by adding benzoyl chloride and the excess monomeric hexamethylene diisocyanate is then separated off by means of a thin film evaporator under reduced pressure, at about 1 mm HG. The heating medium used for the distillation circulated at about 180°C. A yellowish polyisocyanate containing isocyanurate groups is obtained. 10

The nature and amount of the adduct according to the invention, which was prepared from 1,3,5-tris-(N,N-dimethylaminopropyl)-s-hexahydrotriazine (HHT), and the NCO contents of the reaction mixture as a function of the reaction time are shown in Table 4. The reaction is stopped, at the desired NCO content, by adding benzoyl chloride. 15

As a comparative example, hexamethylene diisocyanate was also trimerized in the presence of a co-catalyst system consisting of a mixture of 1,3,5-tris-(N,N-dimethylaminopropyl)-hexahydrotriazine and 6 moles of acetic acid. The comparative example shows that the trimerization takes place substantially more slowly if, instead of the adduct, the individual components are used as such. 20

Table 4  
Trimerization of hexamethylene diisocyanate:  
Example Adduct Nature

		Amount [g]	corresponding amount of pure HHT	NCO 1 [%]	content 4 [%]	after 6 hours [%]
25	HHT . 6 acetic acid	3.7	1.85	38	29.5	25.5
26	HHT . 6 2-ethyl hexanoic acid	3.4	0.92	43.3	31.2	27.2
27	HHT . 6 2-ethyl hexanoic acid	6.8	1.85	28.9	25.6	—
28	HHT . 6 benzoic acid	2.8	0.9*	47.2	35.0	27.8
29	HHT . 6 benzoic acid	4.9	1.8*	45.8	26.4	23.2
30	HHT . 6 2,4,6-trichlorophenol	4.5	0.9*	28.6	21.6	20.9
Comparative Example	HHT	3.7		45.9	39.2	33.8
Comparative Example	HHT	1.8		47.7	46.1	44.4
Comparative Example	co-catalyst system consisting of HHT and acetic acid	1.8 1.9	1.8	43.9	39.6	39

\*in dimethylformamide

## WHAT WE CLAIM IS:

1. An adduct of
  - a) one mole of 1,3,5-tris-(N,N-dialkylaminoalkyl)-s-hexahydrotriazine and
  - b) from 5.5 to 6 equivalents of OH-acidic organic compound having a pKa of from 3 to 10 measured at 20° to 25°C.
2. An adduct as claimed in claim 1, wherein 1,3,5-tris-(N,N-dimethylaminopropyl)-s-hexahydrotriazine is used as the 1,3,5-tris-(N,N-dialkylaminoalkyl)-s-hexahydrotriazine.
3. An adduct as claimed in claim 1 or 2, wherein an organic carboxylic acid or a nitro-substituted and/or halogen-substituted phenol is used as the OH-acidic compound having a pKa of from 3 to 10.
4. An adduct as claimed in claim 3, wherein an aliphatic and/or aromatic monocarboxylic acid and/or dicarboxylic acid is used as the OH-acidic compound.
5. An adduct as claimed in claim 4, wherein the aliphatic monocarboxylic acid is formic acid or acetic acid and the aromatic monocarboxylic acid is benzoic acid.
6. An adduct as claimed in claim 3, wherein 2,4,6-trichlorophenol is used as the OH-acidic compound.
7. An adduct as claimed in claim 1, of one mole of 1,3,5-tris-(N,N-dimethylaminopropyl)-s-hexahydrotriazine and 6 moles of acetic acid.
8. An adduct as claimed in claim 1 and substantially as hereinbefore described or exemplified.
9. A process for the manufacture of an adduct as claimed in claim 1, wherein 1 mole of a 1,3,5-tris-(N,N-dialkylaminoalkyl)-s-hexahydrotriazine is mixed with from 5.5 to 6 equivalents of an OH-acidic compound having a pKa of from 3 to 10 measured at 20° to 25°C, at from 0 to 60°C, in the absence or presence of a solvent which is inert under the reaction conditions.
10. A process for the manufacture of a polyisocyanurate foam, which contains urethane groups and may or may not be of low flammability, by reacting an organic polyisocyanate and a polyol in the presence of a catalyst and in the presence or absence of a blowing agent and other auxiliaries and additives, wherein the catalyst used comprises an adduct as claimed in any of claims 1 to 8.
11. A process as claimed in claim 10, wherein from 1 to 3 parts by weight of the adduct are used per 100 parts by weight of the organic polyisocyanate.
12. A process as claimed in claim 10 or 11, wherein an additional catalyst selected from tertiary amines and organo metal compounds which accelerate the formation of polyurethanes from polyols and polyisocyanates is also employed.
13. A process for the manufacture of a polyisocyanate containing isocyanurate groups by trimerizing or polymerizing an aliphatic and/or aromatic polyisocyanate in the presence of a catalyst which is an adduct as claimed in any of claims 1 to 8.
14. A process as claimed in claim 13, wherein the polyisocyanate is a diisocyanate and from 1 to 3 parts by weight of the adduct are used per 100 parts by weight of the organic diisocyanate.
15. A process as claimed in claim 10 or 13 carried out substantially as described in any of the foregoing Examples.
16. Polyisocyanurate foams when manufactured by a process as claimed in any of claims 10 to 12 or 15.
17. Polyisocyanates when manufactured by a process as claimed in any of claims 13 to 15.

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